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Microwave-assisted extraction of lime pectin ☆

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Abstract

Pectin was extracted from lime flavedo, albedo and pulp by employing microwave-assisted extraction (MAE) under pressure. Heating times ranged from 1 to 10 min. Optimal time of heating was 3 min. Molar mass, viscosity, radius of gyration and hydrated radius were found to decrease with heating time. At 3 min heating time, depending on the lime fraction which was extracted, weight average molar mass ranged from about 310,000 to 515,000 Da, and weight average intrinsic viscosities ranged from about 9.5 to 13 dL/g. Pectins dissolved in 0.05 sodium nitrate were characterized by HPSEC with online light scattering, dynamic light scattering and viscosity detection. Molar mass polydispersity passed through maximum at 4 min. Molecules of pectin became less compact with increasing heating time. The results obtained here are consistent with previous evidence that extracted pectins may exist in solution as networks, partially formed networks, i.e. branched molecules or linear molecules depending on extraction conditions and the solvent in which they are dissolved.
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Keywords: Lime pectin; Microwave; HPSEC; Light scattering; Viscosity; Molar mass; Radius of gyration; Hydrated radius

1. Introduction

Pectin is a polysaccharide consisting mostly of two moieties (Carpita & McCann, 2000). These are homogalacturonan, (1→4) linked, α-D-galacturonic acid and its methyl ester; and rhamnogalacturonan I, (1→2) repeating linked, α-L-rhamnose-(1→4) α-D-galacturonic acid disaccharide. Rhamnogalacturonan I contains arabinan, galactan and arabinogalactan side chains. These monosaccharide units comprise most of sugar units found in pectin.

Pectin is found ubiquitously in the epicarp (flavedo), mesocarp (albedo) and endocarp (edible portion) of the lime. After the juice is squeezed out of the lime, the insoluble material which remains is called pulp. Previously, we have determined the weight average molar mass (M_w) and intrinsic viscosity [η_w] and the z-average radius of gyration (R_{gz}) as a function of heating time for the microwave-assisted extraction (MAE) of pectin from lime albedo (Fishman, Chau, Coffin, & Hotchkiss, 2003). Changes in M_w, η_w and molecular shape with heating time could be rationalized by the hypothesis that continued heating of pectin caused the disaggregation of pectin networks into its component parts.

Typically, in pectin manufacture by the food industry, the whole peel is extracted (Braddock, 1999). In this study we fractionated limes into flavedo, albedo and pulp with the juice and seeds removed. The pectin molecular properties from each fraction were characterized by HPSEC with online static and dynamic light scattering (DLS) and viscosity detection. Also galacturonate, degree of methyl esterification and neutral sugar content were determined for each fraction. In addition, pectin from the albedo was characterized by offline multiangle DLS.

2. Methods

2.1. Materials

Fresh flavedo, albedo and pulp were obtained from tropical seedless limes which were grown in Florida. Upon

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arrival, the flavedo was stripped from the skin with a potato peeler, followed by removal of the albedo with a paring knife. The juice was separated from the pulp by placing the endocarp in an electric juicer. The particle sizes of the flavedo, albedo and pulp were reduced by grinding in a Cuisinart mini prep plus processor. Prior to extraction, the pulp was washed three times with 1 L of HPLC-grade water per 100 g of pulp to remove extraneous material which might be present. Excess water was removed by squeezing it out through miracloth. The washed pulp was stored in sealed polyethylene bags at −20 °C until extraction.

2.2. Extraction

Lime pectin was extracted by a patented MAE procedure (Fishman & Chau, 2000; Fishman, Chau, Hoagland, & Ayyad, 2000). Samples were heated in a CEM, model MDS-2000 microwave oven. Flavedo, albedo or pulp (F, A or P) was irradiated at a frequency of 2450 MHZ with 630 W of power. The slurried sample (1 g) was dispersed in 25 mL of pH 2, HCl and placed in each of six microwave transparent pressure vessels. One vessel was equipped with devices which sensed and controlled pressure and temperature. Heating times ranged from 1 to 10 min. Pressures were not allowed to exceed 50 ± 2 lbs/in^2. The temperature at that pressure was about 140 °C. The change of temperature and pressure with heating time has been published previously (Fishman, Chau et al., 2003). After heating, the samples were allowed to cool for half an hour at room temperature and filtered through miracloth. The filtrate was precipitated with 70% isopropanol (IPA), separated from the mother liquor, washed first with 70% IPA followed by 100% IPA. Then, the sample was dried under vacuum without heating and stored in a refrigerator until analyzed.

2.3. Chromatography

Dry sample (2 mg/mL) was dissolved in mobile phase (0.05 M $NaNO_3$), centrifuged at 50,000 g for 10 min and filtered through a 0.22 or 0.45 μm Millex HV filter (Millipore Corp., Bedford, MA). The flow rate for the solvent delivery system, model 1100 series degasser, auto sampler and pump (Agilent), was 0.7 mL/min. The injection volume was 200 μL. Samples were run in triplicate. The column set consisted of two PL Aquagel OH-60 and one OH-40 size exclusion columns (Polymer Laboratories, Amhearst, MA) in series. The columns were in a water bath set at 45 °C. Two HPSEC chromatographs were employed. These differed only in the column effluent detectors used. One chromatograph was fitted with a Dawn DSP multi-angle laser light scattering photometer (MALLS) (Wyatt Technology, Santa Barbara, CA), model 100 differential pressure viscometer (DPV) (Viscotek Corp., Houston TX) and an Optilab DSP interferometer (RI) (Wyatt Technology). Electronic outputs from the 90° light scattering angle, DPV and RI were sent to one directory of a computer for processing with TRISEC software (Viscotek Corp.). Electronic outputs from all the scattering angles measured by the MALLS, DPV and RI were sent to a second directory for processing with ASTRA™ software (Wyatt Technology). The other chromatograph was fitted with a model PD2020/DLS two-angle static light scattering photometer (TALLS) (Precision Detectors, Franklin, MA) installed in a model 2410 differential refractometer (RI) (Waters Inc., Milford, MA). The PD2020 was also fitted with add on, 90° DLS module permitting simultaneous measurement of static and DLS. The electronic outputs from the RI, static and DLS modules were sent to a computer and processed by PrecisionAcquire32 and PrecisionAnalyze software.

2.4. Multi-angle DLS

Offline, batch-mode multiangle DLS measurements have been described previously (Farrell et al., 1996). Briefly, measurements were with a Malvern System Model 4700c equipped with a 256-channel correlator. Light at 488 nm was generated by a Spectra Physics Model 2020, 5-W laser. DLS measurements were made at 30°, 60°, 90°, 120° and 150°. The data were processed by Malvern Automeasure, V. 4.12 software. Multi-angle analysis was performed with Malvern software (Cummings & Staples, 1987). System performance and analysis software were tested on 91 and 455 nm diameter beads and found to be accurate within ±2%.

2.5. Compositional analysis

Anhydrogalacturonate content (%G) was determined by the Sulfamate/3-Phenylphenol Colorimetric Method (Filli-setti-Cozzi & Carpita, 1991) as modified by Yoo, Fishman, Savary, and Hotchkiss Jr. (2003). Degree of methyl esterification (%DE) was determined by an HPLC method developed by Voragen, Schols, and Pilnik (1986). Neutral sugar content (%NS) was determined with the Phenol-Sulfuric Acid Colorimetric Method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956).

3. Results and discussion

3.1. Basis of MAE

In general, advantages of MAE of pectin in a closed vessel include rapid heating time (localized super heating), control of temperature and pressure, higher temperatures, higher pressures and negligible volatility of solvents.

The kinetics of heating for samples extracted by microwave energy is determined by the tan δ of the sample. Tan δ is the ratio of the dielectric loss, ε″, to dielectric constant, ε′, of the sample (Ness & Collins, 1988).

$$\tan \delta = \varepsilon''/\varepsilon'. \quad (1)$$

The value of ε' is a measure of a sample's ability to obstruct microwave energy as it passes through the sample whereas ε'' is a measure of a sample's ability to dissipate that energy (i.e. convert electromagnetic energy into heat energy). Ionic conduction and dipole rotation are the most important mechanisms for producing dielectric loss. Thus, the speed of heating increases with increasing rapidity of dipole rotation and ionic conduction.

Preliminary experiments on albedo dispersed in pure water, revealed that no pectin could be extracted by MAE under pressure (data not shown). These experiments appear to indicate that rapid MAE of pectin occurs by conventional acid extraction. Heated acid solubilizes pectin and other components held in the cell wall. First, relatively weak forces such as ionic or hydrogen bonds are broken, followed by covalent bonds such as glycosidic linkages. Acid also hydrolyzes pendent ester groups attached to pectin. Rapid rotation of water dipoles coupled with the ionic conductance of H^+ and Cl^- ions provides a solvent with high dielectric loss capable of being rapidly heated. The advantage of rapid heating and extraction (minutes) over conventional slow extraction (i.e. half an hour or longer) is that fewer co-valent bonds are broken. This in turn produces pectin with higher molar mass and viscosity (Fishman, Chau et al., 2000; Fishman, Chau, Kolpak, & Brady, 2001). As further evidence for support of the rapid heating hypothesis, high molar mass and viscosity pectin can be obtained by extracting pectin under conditions of rapid heating under pressure by steam injection (Fishman, Walker, Chau, & Hotchkiss, 2003).

We also conducted preliminary studies (data not shown) on the effect of pH at the start of heating on the molar mass and intrinsic viscosity of the pectin extracted. The heating time was 3 min. We found that yield was inversely related to increasing the pH from 1 to 3 whereas molar mass and intrinsic viscosity was increased more or less proportionately with increasing pH. Thus we chose pH 2 to obtain optimal yield with high molar mass and intrinsic viscosity.

3.2. Dry matter and pectin distribution of fractions

Table 1 contains the wet and dry weight of the three lime fractions. About 71% of the lime is volatile under vacuum. The albedo contains about 40% dry matter whereas the flavedo contains about 36% and the flavedo about 21%. Table 2 contains pectin recovered as percentage of the dry weight of the starting material. The relatively low percentages of dry weight and pectin in the flavedo are probably due to a significant amount of volatile organics in that tissue.

3.3. Anhydo-galacturonate and neutral sugar composition of albedo, flavedo and pulp

The compositional data for albedo, pulp and flavedo are in Table 3. There appears to be no consistent trends with time of heating or fraction for the variables measured. Thus, over the time range of 2.5–10 min, compositional values appear to be independent of extraction time. The mean percentages are: neutral sugar (%NS), 7–10, anhydrogalacturonic acid (%G), 84–89 and degree of methylesterification %DE, 59–75.

Table 1
Weight distribution of fractions

Fraction	Wet weight (g)	Dry weight (g)	% Dry weight
Albedo	66.65	26.52	39.78
Pulp	134.2	28.28	21.07
Flavedo	60.35	21.73	36.01
Total	261.2	76.53	96.86

Table 2
Weight percentage of pectin recovered

Time (min)	Albedo	Pulp	Flavedo	Total
2.5	6.2 (0.1)[a]	6.0 (0.1)	1.1 (0.5)	13.1(1.0)
3.0	5.1 (0.8)	8.2	1.3 (0.2)	14.6
4.0	4.6 (0.8)	10.0	3.8 (3.3)	17.9
6	5.2	3.4 (1.0)	3.2 (0.2)	11.8
10	2.3 (0.4)	3.4 (0.9)	2.1 (0.3)	8.0(1.0)

[a]Standard deviation of triplicate analysis.

3.4. Molecular properties of albedo, flavedo and pulp

Previously, Fishman et al.(2001) found that pectins tended to be somewhat less aggregated in lithium acetate/acetic acid buffer than in $NaNO_3$ solution. In $NaNO_3$, the molar mass of pectin is about 10–20% larger for high methoxyl pectin than for pectin in the lithium buffer. Unfortunately, over a period of time, the lithium buffer, unlike $NaNO_3$, was found to corrode the stainless steel capillaries of the on-line viscometer detector. Since the simultaneous measurement of intrinsic viscosity and molar mass was considered to be essential in studying changes in aggregation, we chose to abandon the lithium buffer in favor of $NaNO_3$. Furthermore, as is shown in this study and in two others (Fishman, Chau et al., 2003; Fishman, Chau et al., 2000), the molar mass of less aggregated high methoxyl pectin is appreciably lower than 280,000 found with use of the lithium buffer system. Thus, the somewhat higher value obtained in $NaNO_3$ over lithium buffer should not affect conclusions concerning the structure of less aggregated pectin.

Molar masses (M) and radii of gyration (R_g) were determined by three different methods involving online static light scattering in conjunction with HPSEC. The LSV method combines light scattered at one angle (90°) and online viscometry to obtain M and R_g (Fishman, Doner, Chau, & Hoagland, 2000), TALLS uses light scattered at two angles (90° and 15°) (Mourey & Coll,

Table 3
Composition of pectin

Time (min)	Albedo			Pulp			Flavedo		
	%DE[a]	%G[b]	%NS[c]	%DE	%G	%NS	%DE	%G	%NS
2.5	66 (1)[d]	88 (2)	6 (1)	88 (1)	72 (2)	9 (1)	70 (1)	81 (1)	11 (1)
3	64 (1)	89 (2)	11 (1)	58 (1)	92 (4)	5 (1)	59 (1)	88 (4)	13 (2)
4	66 (1)	86 (2)	8 (1)	79 (1)	80 (6)	10 (1)	53 (2)	92 (3)	5 (1)
6	73 (1)	85 (4)	10 (1)	87 (1)	81 (4)	8 (1)	56 (2)	89 (6)	12 (1)
10	72 (1)	91 (3)	9 (1)	65 (1)	93 (11)	5 (1)	56 (1)	94 (2)	10 (1)
Mean	68 (4)	88 (2)	9 (2)	75 (13)	84 (9)	7 (2)	59 (7)	89 (5)	10 (3)

[a]Pecentage degree of methylesterification.
[b]Percentage anhydrogalacturonate.
[c]Percentage neutral sugars.
[d]Standard deviation of triplicate analysis.

Table 4
Molar masses of lime fractions[a]

Time (min.)	Albedo		Pulp		Flavedo	
	$M_w \times 10^{-3}$	M_w/M_n	$M_w \times 10^{-3}$	M_w/M_n	$M_w \times 10^{-3}$	M_w/M_n
2.5	335 (8)[b]	1.31 (0.01)	559 (7)	1.13 (0.01)	354 (4)	1.47 (0.03)
3	311 (1)	1.38 (0.03)	515 (3)	1.15 (0.01)	310 (1)	1.61 (0.05)
4	96.9 (1)	1.90 (0.05)	163 (4)	1.42 (0.01)	188 (2)	1.86 (0.04)
6	28.1 (0.2)	1.41 (0.02)	34.7 (0.7)	1.40 (0.05)	42.8 (3)	1.82 (0.3)
10	16.5 (0.3)	1.27 (0.01)	13.0 (0.7)	1.10 (0.01)	17.1 (0.4)	1.38 (0.06)

[a]Measured by MALLS.
[b]Standard deviation of triplicate analysis.

1995), and MALLS uses light scattered at 16 angles (14.4°, 25.9°, 34.8°, 42.8°, 51.5°, 60.0°, 69.3°, 79.7°, 90.0°, 100.3°, 110.7°, 121.2°, 132.2°, 142.5°, 152.6° and 163.3°) (Wyatt, 1993).

All three methods showed that molar mass decreased with time of heating. M_w values measured by the MALLS method are in Table 4. When the weight average molar mass (M_w) was below 10^5, all three methods gave about the same values for M_w. In the range $1–2 \times 10^5$, values from MALLS and LSV were in good agreement but values from TALLS were problematical. In that range TALLS values were found to be higher, lower or about the same as MALLS values. Above 2×10^5, MW values from LSV were found to be higher than MALLS values whereas TALLS values were found to be lower except in one case where there was good agreement between TALLS and MALLS values.

In Fig. 1, M_w is plotted against heating time during extraction. As mentioned above, molar mass decreased with increasing heating time, for all three fractions. Pulp had a substantially higher molar mass than the other two fractions at heating times of 2.5 and 3 min. At heating times of 4 min or more, molar masses for all three fractions were fairly close. As shown by the data in Table 4 and Fig. 2, the pulp had the lowest polydispersity (M_w/M_n) in the heating range of 2.5–4 min and the lowest molar mass

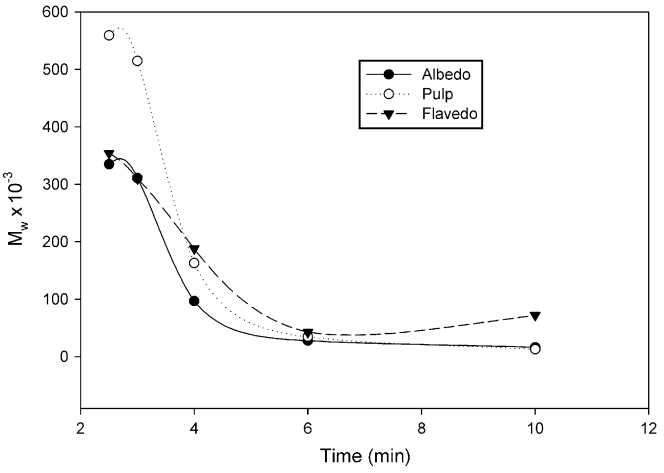

Fig. 1. Dependence of molar mass on heating time for pectin from the albedo, pulp and flavedo.

at 10 min of heating. Furthermore, the polydispersity passes through a maximum with heating time for the three fractions. These results are consistent with a previous extraction study (Fishman, Chau et al., 2003) which indicates that at heating times of less than 3 min, extracted pectin is high in molar mass, aggregated and narrow in polydispersity. As heating time increases beyond 2.5 min,

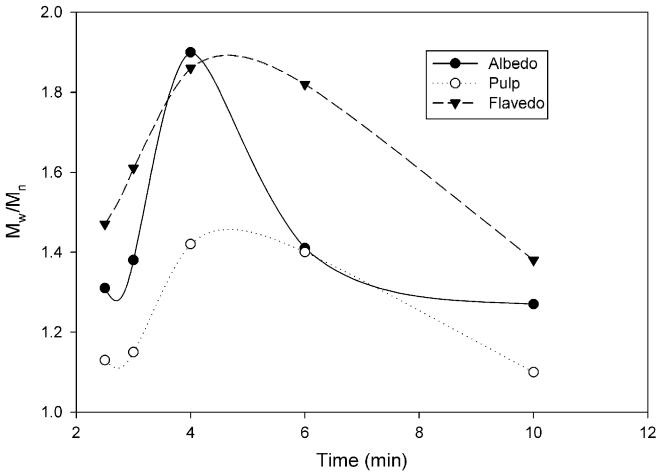

Fig. 2. Dependence of polydispersity of molar mass on heating time for pectin from the albedo, pulp and flavedo.

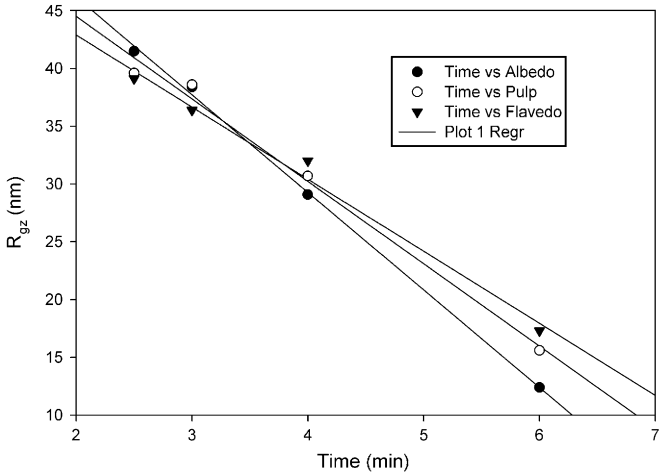

Fig. 4. Dependence of radius of gyration on heating time for pectin from the albedo, pulp and flavedo.

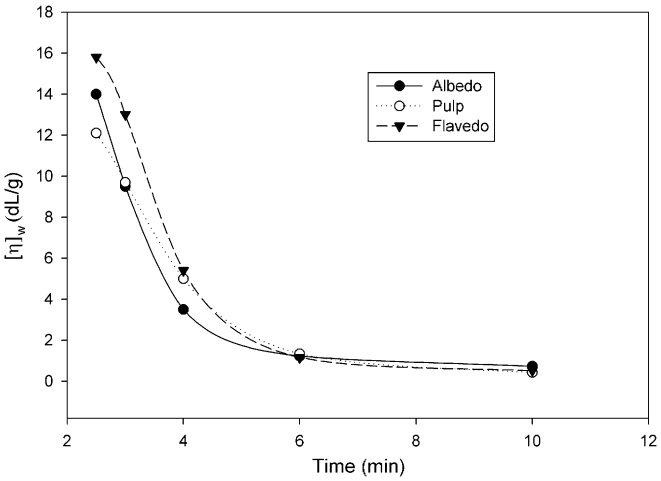

Fig. 3. Dependence of intrinsic viscosity on heating time for pectin from the albedo, pulp and flavedo.

pectin which is in solution is dissociated. The polydispersity broadens as mixtures of different sized aggregates form and reach a maximum between 4 and 5 min. Upon further heating, the aggregates are broken down into their component parts which are of comparable size. After 10 min of heating, mostly component parts are present and distributions are once again narrow.

It is of interest to note that unlike conventional methods of extraction, microwave extraction under pressure, produces high methoxyl pectin with a wide range of molar masses (see Tables 3 and 4).

Intrinsic viscosities, ($[\eta]_w$), are plotted against time of heating for the three lime fractions (Fig. 3). At 3 min heating time, the order of $[\eta]_w$ values was flavedo > pulp = albedo. As was the case with M_w, there is a large decline in $[\eta]_w$ between 2.5 and 4 min.

The radii of gyration (R_{gz}) for the three lime fractions measured by MALLS are plotted against time in Fig. 4. R_{gz} follows a first-order linear regression with heating time. All three lines have correlation coefficients of 0.99 or greater. At 3 min heating time, the order of R_{gz} values is pulp = albedo > flavedo. At 10 min R_{gz} values were too small to be measured by MALLS.

Fig. 5A–C are Mark–Houwink (M–H) plots at heating times ranging from 2.5 to 10 min for albedo, pulp and flavedo. These data were obtained by the LSV method. Previously we have shown for orange pectin obtained by steam injection, that there was a linear correlation between M_w values obtained by the LSV method and the MALLS method (Fishman, Walker et al., 2003). Furthermore, the LSV method gave higher M_w values than the MALLS method. Nevertheless, because of the linear correlation between the two sets of M_w values, we expect that the slope of the M–H plots would be fairly independent of the set of molar mass values which were used. Only the intercepts might differ significantly. In Fig. 6, we have plotted M_w from the LSV method against M_w from the MALLS method. Again, we have found a high linear correlation between the two M values (i.e. $r^2 = 0.96$). The only difference between this study and the previous one was that the slope in Fig. 6 was 1.57 rather than 3 which was found previously. A possible explanation for this difference in slopes is that there is a higher heterogeneity in molecular shapes for extracted pectins from orange than there is for extracted lime pectins. Previously, we have found that orange pectin is more highly branched than lime pectin (Fishman, Chau et al., 2003) and that the M_w values from the LSV method tend to diverge from M_w values from the MALLS method for samples which are mixtures of heterogeneous shapes (Fishman, Walker et al., 2003). In Fig. 5, the aggregate plots for each fraction show a downward curvature over the entire heating range indicating the presence of more than one shape. Also, as the heating time increases, the molar masses of the distribution cover a lower range of M_w values. In Fig. 7, the M–H exponents against M_w obtained from MALLS for the pectin in the three plant fractions. The data in Fig. 7

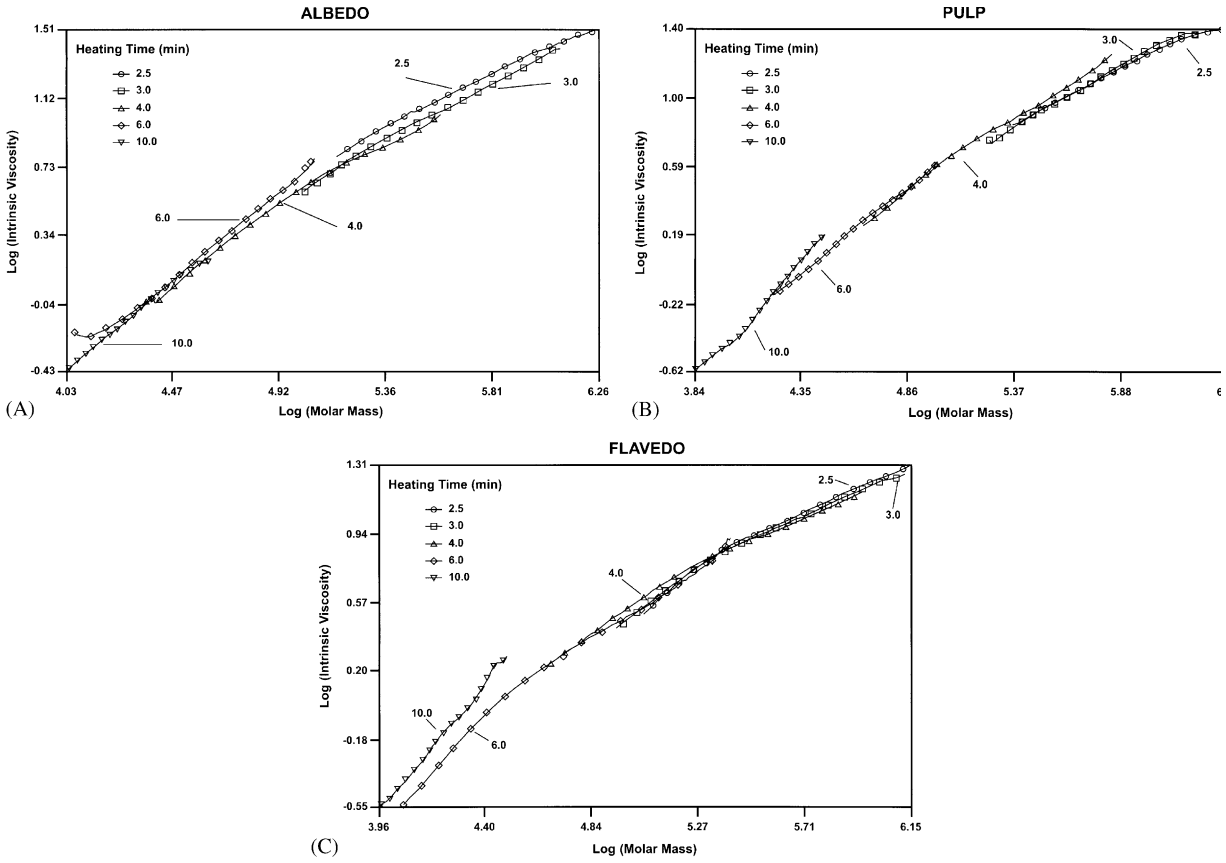

Fig. 5. (A) Dependence of Mark–Houwink (M–H) plots on heating time for pectin from the albedo, (B) dependence of M–H plots on heating time for pectin from the pulp and (C) dependence of M–H plots on heating time for pectin from the flavedo.

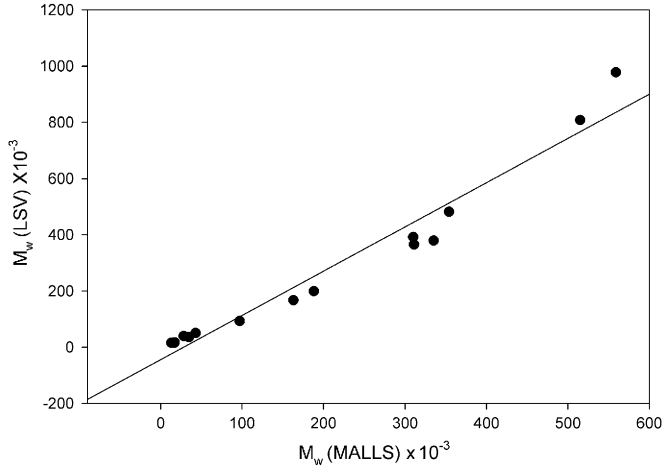

Fig. 6. Correlation of molar mass between MALLS and LSV methods for obtaining molar mass.

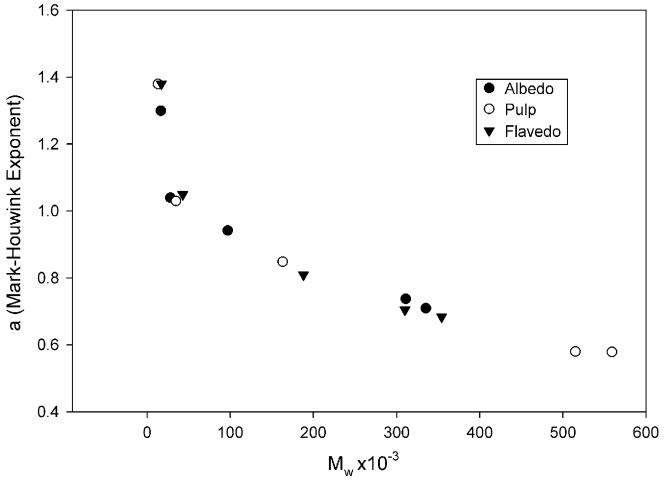

Fig. 7. Dependence of Mark–Houwink exponents on molar mass for pectins from the albedo, pulp and flavedo.

revealed that the "*a*" values decrease with increasing M_w. This trend is consistent with the concept that the aggregates tend to occupy less space per unit of molar mass than the partially or fully dissociated components of the aggregates. Furthermore, the data are consistent with concepts obtained from electron microscope images (Fishman, Cooke, Hotchkiss, & Damert, 1993; Fishman, Cooke, Levaj, & Gillespie, 1992). Namely, that pectin can exist in solution as networks, partially formed networks (i.e. branched molecules) and linear molecules (i.e. rods, segmented rods and kinked rods). In fact, this progression of states is the reverse of network formation as described for polymer gels (deGennes, 1979).

In Fig. 8, we have constructed a dynamic Zimm plot, by plotting the *z*-average hydrated molecular diameter obtained from DLS measurements of albedo pectin heated

for 2.5 min (2 × hydrated radius, R_{hz}) against the sum of the angular dependence of scattering and the pectin concentration dependence (Chapman, Morris, Selvendran, & O'Neill, 1987). The concentrations in mg/mL are given at the bottom of the lattice and the scattering angles to the right of the lattice.

The value of the hydrated radius of a macromolecule can be obtained from changes in light scattered from dilute solution with time because Brownian motion causes local concentration fluctuations of dissolved molecules. When visible light impinges on these solutions, under certain conditions, the light is absorbed and reemitted (scattered) by the dissolved molecules. If the intensity of light due to these fluctuations is measured as a function of time, the translational diffusion constant, D, for that molecule can be obtained (Burchard, 1996). The Stokes–Einstein equation relates D and R_h, according to Eq. (2)

$$D = kT/(6\pi\eta_o R_h). \quad (2)$$

Here, k is the Boltzman constant, T is absolute temperature and η_o is viscosity of the solvent.

The weight average molar mass of the pectin heated for 2.5 min is 3.35×10^5. For this same sample, the polydispersity ratios M_w/M_n and M_z/M_n are 1.31 and 1.75, respectively; and the R_{gz} value is 41.5 nm. Simultaneous extrapolation of scattering angle and concentration to zero, gives a value of 321.8 nm for the hydrated diameter or a value of 160.9 for the value of R_{hz}. The ratio of R_{gz}/R_{hz} is symbolized by ρ. This value is 0.26 for the pectin which was heated for 2.5 min. The value of ρ for a cross-linked microgel with branches is 0.6, a homogeneous sphere is 0.778, a random coil is 1.5–2.05 depending on polydispersity and goodness of solvent, a rigid rod is >2 (Burchard, 1996). The rather low value of ρ, may be due to the presence of a very small quantity aggregated pectic fragments which would raise the value of R_{hz}. The value of the hydrated diameter obtained by extrapolating the data obtained from light scattered at 90° is 103.4 nm and R_{hz} is 51.7 nm. A ρ value of 0.87 is obtained using 41.5 as R_{gz}. This value of ρ is consistent with earlier findings that pectin obtained by rapid MAE is in the form of a partially formed network, i.e. branched. The rationale for taking the R_{hz} value at 90° rather than the value extrapolated to 0° is that the 90° value should be less sensitive to trace amounts of large aggregates which may be present. Table 5 contains values of R_{hz} obtained at 90° from the online DLS detector described in Section 2.3 and ρ values using R_{gz} values in that table. The R_{hz} value, 51 nm, for the albedo pectin in Table 5 is about the same as the 90° value obtained from the data shown in Fig. 8. These data were obtained from the stand-alone multiangle DLS detector described in Section 2.3. Based on the M–H exponents obtained (see Fig. 7), it would appear that the ρ values obtained for pectin at 4 and 6 min were too low. Nevertheless, R_{gz} and R_{hz} decreased with M_w as expected.

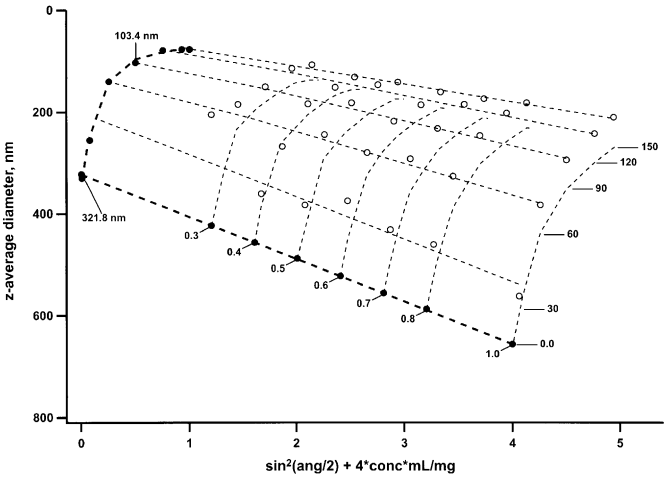

Fig. 8. Dynamic Zimm plot of pectin from albedo heated for 2.5 min.

4. Conclusions

With few exceptions, lime albedo, pulp and flavedo gave similar trends when changes in molar mass, intrinsic viscosity, radius of gyration and hydrated radius were monitored with time of heating during extraction. Molar mass, intrinsic viscosity, radius of gyration and hydrated radius, all decreased with time of heating during extraction. Also, for all three fractions, polydispersity of molar mass exhibited a maximum at 4 min of heating and shapes became less compact as heating times increased. Nevertheless, there were some differences in properties among

Table 5
Radii of lime fractions

Time (min)	Albedo			Pulp			Flavedo		
	R_{gz}[a]	R_{hz}[b]	ρ	R_{gz}	R_{hz}	ρ	R_{gz}	R_{hz}	ρ
2.5	41.5 (1.0)[c]	51 (1)	0.82	39.6 (0.2)	51 (1)	0.78	39.1 (0.1)	49 (1)	0.80
3	38.4 (0.5)	55 (3)	0.69	38.6 (0.1)	49 (1)	0.80	36.4 (1)	44 (1)	0.82
4	29.1 (0.8)	44 (1)	0.65	30.7 (0.2)	35 (1)	0.88	32.0 (1)	32 (1)	1.0
6	12.4 (2)	12 (2)	1.0	15.6 (2)	23 (1)	0.70	17.3 (3)	28 (7)	0.6

[a] R_{gz} (MALLS).
[b] R_{hz} (90°).
[c] Standard deviation of triplicate analysis.

fractions at specific times of heating. All these observations can be rationalized by the hypothesis that lime pectin is extracted as a mixture of networks, partially formed networks and components thereof. The relative amounts of these various moieties depend upon the time of heating.

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